

Morphology of Polyaniline Redoped by Kneading with Dodecylbenzene Sulfonic Acid

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ABSTRACT: Polyaniline (PANI) is often doped with an inorganic acid, which can be removed in a dedoping process with ammonium hydroxide and then replaced with an organic acid in a redoping process. This article shows that both the developing and redoping processes are influenced by the morphology of the PANI aggregates containing the primary particles. The detailed morphology develops during the aniline polymerization step and may vary from closed to open structures, depending on the polymerization conditions. The redoping process under mild conditions (manual kneading at 20–60°C) with dodecylbenzene sulfonic acid (DBSA) leads to the formation of a DBSA-rich surface layer covering the aggregates, which consists of fully doped PANI-DBSA and free DBSA. The thin conductive PANI-DBSA layers surrounding the aggregates form a continuous conducting network in compression-molded samples. The depth of penetration of DBSA molecules into the PANI-base aggregates obviously depends on the aggregates structure, that is, a higher DBSA penetration and, thus, a more continuous PANI-DBSA outer layer for the open structures. © 1998 John Wiley & Sons, Inc. *J Appl Polym Sci* 69: 2205–2212, 1998

Key words: polyaniline; redoping; electrically conductive polymers

INTRODUCTION

Polyaniline (PANI) is one of the most promising intrinsically conducting polymers due to its straightforward polymerization, chemical stability, and relative high conductivity.^{1,2} PANI is commonly available as a powder of an emeraldine salt doped with a mineral acid, which is not processable. The redoping of PANI with functionalized protonic acids, for example, organic sulfonic acids or disubstituted hydrogen phosphates, to improve its processability is the topic of numerous publications.^{3–6}

The starting material in the redoping process

is the undoped or base form of PANI. The PANI-base characteristics, including molecular structure and particle morphology, are strongly influenced by the method and conditions at which the PANI-salt was synthesized (stirrer speed, temperature, acidity, aniline-acid-water-oxidant proportions, accelerating additives, surfactant used, size of reactor flask, etc.).^{2,3,7,8–11} Evidently, the usual polymerization route,² carried out in different laboratories, has yielded PANI powders of different properties. For example, a color ranging from violet to deep blue, purple-red, or brown was reported for undoped powders. The dedoping level, namely, the mole fraction of acid removed, was reported between 0.3–0.5, rather than the maximal value of 0.5.^{12–14} PANI can achieve its highly conductive state through the protonation of the imine nitrogen atoms in its emeraldine (EM)

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oxidation state. Hence, the redoped state of PANI depends on the replaced acid molar fraction, which may equal the amount of acid removed from the pristine PANI salt.

Most recent studies focused on redoping processes of PANI-base with organic dopants of relatively large molecular size, for example, camphor-sulfonic, or dodecylbenzene sulfonic acids, and alkyl- and aryl-substituted hydrogen phosphates. A relatively high conductivity level of redoped PANI was achieved even at low molar fractions of dopant, less than the fully doped state.¹⁵⁻¹⁹ It was found that only a certain fraction of the dodecylbenzene sulfonic acid (DBSA) added during the redoping process penetrates into the particles of the PANI-powder, and, therefore, an elevated temperature was required to somewhat increase the doping and the conductivity levels.^{13,15} Thus, in addition to the chemical structure, the particle structure of PANI-base is an important factor determining the amount of dopant penetrating into the PANI particles, especially the dopants of large molecular size. For example,²⁰ the lack of porosity in a cast PANI-base film limits the doping accessibility of DBSA molecules, resulting in a low level of doping and excess DBSA at the film's surface. Morphological changes providing an open film structure enhance both the doping level and its rate. The specific redoping procedure by itself may also play a key role. Solution or melt doping procedures, following an initial room temperature blending of a PANI-base powder with an organic acid,^{3,13,21,22} results in several concurrent conformational and morphological changes in the PANI. In processing of a PANI powder with a dopant solution,^{13-16,23} the solvents used may interfere with the doping process. Solvents such as substituted benzenes, chloroform, and *m*-cresol can dissolve a portion of the doped complex formed, whereas ethanol has the capacity of H-bonding.

The objective of the present study is to investigate the effect of kneading of liquid DBSA with PANI-base powders having different particle structures and to elucidate the structure of the doped particles.

EXPERIMENTAL

Polyaniline was produced by a chemical oxidation polymerization on a pilot-plant scale, using an aqueous sulfuric acid medium and ammonium persulphate as an oxidant, yielding batches of 1–1.2 kg.²⁴ PANI-base powder was prepared by de-

doping the PANI-H₂SO₄ salt powder with ammonium hydroxide (1 wt % aqueous solution) in a stirred reactor for 3 h. The dedoped material was filtered, rinsed with water and acetone, and finally dried under vacuum at 60°C to give a brown-violet powder. The weight loss due to the dedoping process was in agreement with the initial 1 to 0.32–0.33 PANI-to-H₂SO₄ molar ratio (Table I). Since the dedoped PANI-base powder could not be fully dissolved in a concentrated (98.5 wt %) sulfuric acid, it probably consists of some branched or lightly crosslinked chains. For comparison purposes, a commercial doped PANI, Versicon[®] (Ormecon Chemie, Ammersbek, Germany), was also dedoped by the same procedure. According to the weight loss, assuming paratoluene sulfonic acid (*p*-TSA) as the dopant, a 1 to 0.34 PANI-to-*p*-TSA molar ratio was calculated (Table I), in agreement with the literature.¹⁴

A sample of dry PANI-base powder was mixed at room temperature with a known quantity of DBSA (technical grade) for 5 min and subsequently heated in a vacuum oven at 60°C for 3 h (hourly repeated mixing). Heat generation and color change of the powder during the initial mixing step prior to heating was observed. A series of partially doped powdery samples was prepared by successive addition of increasing amounts of DBSA. In all cases, the excess DBSA was removed by water rinsing, followed by drying at 60°C under vacuum, until a constant weight has been achieved.¹³

Small plaques of the redoped PANI-DBSA (2.6 × 1.5 × 0.25 cm) were prepared by compression molding at room temperature and 800 atm. The plaque's conductivity was measured by the 4-probe method using a Sorenson power supply and a Keithley Autoranging Electrometer 175.

The PANI-base and PANI-DBSA morphology was studied using a Jeol 5400 scanning electron microscope (SEM). The sulfur content and its distribution within the outer surface layer of the aggregates was studied using a Voyager II energy-dispersive spectroscopy (EDS). Each sample was studied at accelerating voltages of 15 kV (penetration depth of about 2–3 μm) and 5 kV (depth of about 0.2–0.3 μm). It should be noted that in addition to the scatter in EDS data due to the samples surface roughness, the low total sulfur concentration introduces inaccuracy in the EDS data.

RESULTS AND DISCUSSION

The starting materials, 2 selected samples of PANI-H₂SO₄ and PANI-*p*-TSA (Table I), were

Table I Characteristics of the Studied PANI Samples

Pristine PANI–Salt	Doping Level ^a	Conductivity (S/cm)	PANI–Base Appearance
PANI–H ₂ SO ₄ (I)	0.33	0.17	Aggregates open [Fig. 1(a)]
PANI–H ₂ SO ₄ (II)	0.32	0.20	Aggregates closed [Fig. 1(d)]
PANI– <i>p</i> -TSA (Versicon)	0.34	3.75	Aggregates sphere within sphere ²⁵

Doping level is expressed as an acid-to-PANI–base molar ratio determined by dedoping in an aqueous NH₃ (~ 1 wt%).

dark green fine powders, exhibiting a similar doping level but different electrical conductivity values. The difference in conductivity probably stems from the different synthesis conditions of pristine PANI salts in the presence of sulfuric or *p*-toluene sulfonic acids. The different conditions apparently have resulted in different structures, aggregative in nature (Fig. 1)²⁵. Dedoping yielded brown–violet fine powders, which were further used in the present series of experiments. Although the 2 samples of pristine PANI–H₂SO₄, reported in Table I, have a similar doping degree and conductivity, they significantly differ in their particle structure, as in Fig. 1(a) and (d). Both are aggregates (10–100 μm long) of primary particles, about 50–100 nm in size; however, the aggregates of the first PANI–H₂SO₄ sample exhibit an open structure (PANI–OP), contrary to the closed aggregates structure (PANI–CL) of the second PANI–H₂SO₄ sample.

The PANI-to-DBSA molar ratios in the prepared redoped systems (Table II) are similar to the initial doping levels (Table I). However, large differences in the appearance and conductivity of the redoped products were observed for these PANI samples (Table II). PANI–OP, with its open aggregate structure, quickly absorbed the added DBSA and remained dry, and its fine texture [Fig. 1(b)] was preserved, exhibiting a conductivity level similar to that of the pristine PANI sulfate (Tables I and II). In contrast, the mixture of PANI–CL powder with DBSA transformed into a wet powder, exhibiting a surprisingly low conductivity. The latter may be attributed to the low level of DBSA penetration into the aggregates and the excess DBSA observed on the particles surface [Fig. 1(e)], which has been squeezed out under compression molding. The Versicon powder aggregates are characterized by an average grain dimension of about 50 μm consisting of primary tiny spheres of about 100 nm in size.²⁵ The mixture of Versicon–base powder with DBSA transforms upon mixing to blue–green lumps, which are eas-

ily compression molded and exhibit a conductivity level similar to that of the pristine PANI–*p*-TSA (Tables I and II). The kneaded samples were washed with a large excess of water to remove the excess free DBSA. Interestingly, water has the capacity of H-bonding with DBSA, leading to gelation at relatively low DBSA concentrations, which affects the process of DBSA removal with water rinsing. In both PANI–OP and Versicon powders, in which DBSA was quite well absorbed, only relatively small amounts of DBSA were washed away, resulting in a small conductivity reduction (Table II). The water treatment has actually created a gelled DBSA layer, covering the aggregates [Fig. 1(c)]. By contrast, the PANI–CL–DBSA powder turned upon washing practically back to the violet PANI–base state [Fig. 1(f)] with small amounts of DBSA remaining (Table II), exhibiting a low conductivity level even in comparison with that of the unwashed sample. Acetone does not provide H-bonding with DBSA and cannot dissolve both PANI–base and PANI–DBSA complex. The treatment of PANI–OP–DBSA with acetone results in DBSA removal from the aggregates' surface layer and a drastic drop of the conductivity from 0.34 to 4×10^{-5} S/cm (Table II), probably due to disruption of continuity of the doped layer, covering the aggregates.

EDS analysis of sulfur content can yield valuable information regarding the DBSA concentration profile through the surface layers. It enables the examination of a concept of DBSA-rich surface layer structure, that is, partial DBSA penetration. If the DBSA distribution throughout the aggregates were uniform (contrary to the concept of DBSA-rich surface layer structure), the average sulfur content would also represent the aggregates' surface layer. As shown in Table III, the sulfur contents in the surface layer of the water-washed PANI–OP–DBSA and Versicon–DBSA samples are much higher than the calculated values. Moreover, in the case of PANI–OP–DBSA washed sample, the sulfur content decreases with

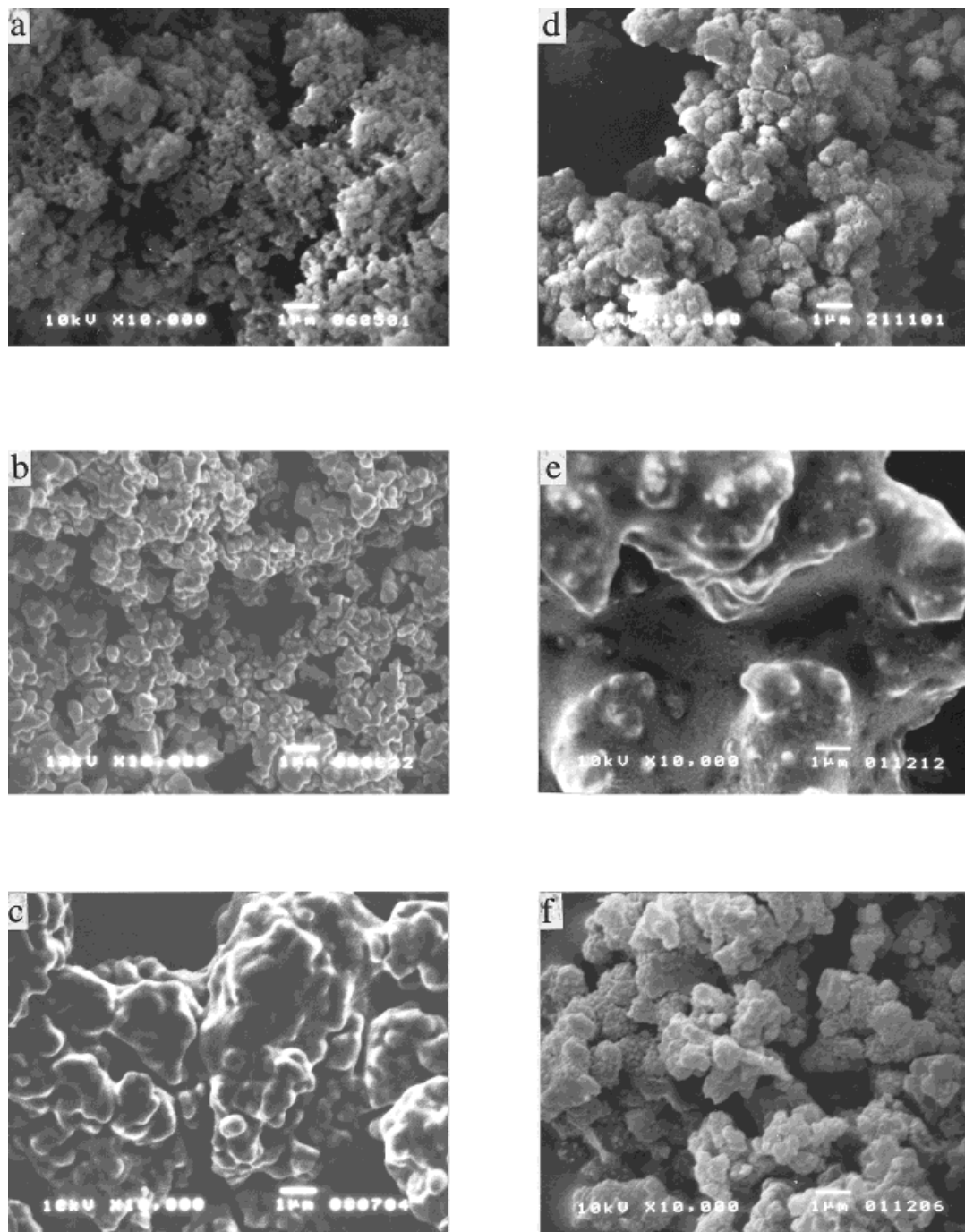


Figure 1 SEM micrographs of (a) PANI-OP-base, (b) PANI-OP-DBSA, (c) water-washed PANI-OP-DBSA, (d) PANI-CL-base, (e) PANI-CL-DBSA, and (f) water-washed PANI-CL-DBSA. The designations correspond with Tables I and II.

increasing the penetration depth, indicating the occurrence of a DBSA-rich surface layer structure. This surface layer, engulfing the PANI-base aggregates, participates in building a continuous conducting network. In fact, the conducting PANI-DBSA complex outer layer may block further

DBSA penetration into the aggregates' bulk, preventing a further conductivity increase.

Interesting information was obtained from analysis of the partially redoped PANI-OP samples, obtained by successive addition of increasing amounts of DBSA (Table IV). The same conduc-

Table II Kneaded PANI–Base–DBSA Mixtures

Sample	PANI-to-DBSA Weight Ratio	PANI-to-DBSA Molar Ratio	Appearance	Conductivity (S/cm)
PANI–OP–DBSA	1 : 1.00	1 : 0.28	Black powder [Fig. 1(b)]	0.34
PANI–OP–DBSA (water-washed)	1 : 0.48	1 : 0.13	Black powder [Fig. 1(c)]	0.12
PANI–OP–DBSA (acetone-washed)	1 : 0.25	1 : 0.06	Black-blue powder	0.00004
PANI–CL–DBSA	1 : 1.25	1 : 0.32	Grey powder wet [Fig. 1(e)]	0.003 ^a
PANI–CL–DBSA (water-washed)	1 : 0.11	1 : 0.03	Violet powder [Fig. 1(f)]	0.0005
Versicon–DBSA	1 : 1.22	1 : 0.30	Blue-green lumps	4.20
Versicon–DBSA (water-washed)	1 : 0.74	1 : 0.21	Blue powder	3.00

^a The excess DBSA was squeezed out under compression molding.

tivity level was measured for the unwashed and water-washed samples (Table IV), even though only a 1 to 0.15 PANI-to-DBSA initial molar ratio was used (PANI-OP-DBSA-1, first kneading). Although the washed sample had a color appearance close to that of PANI-base, scanning electron microscopy (SEM) micrographs showed a smooth coated aggregate surface [Fig. 2(a) and (b)]. EDS data of the washed sample shows (Table III) that at 2- μm depth, the average sulfur content is close to the calculated value (Table III). At an accelerating voltage of 5 kV and 0.3–0.5 μm penetration depth, nonuniformity is observed; that is, a region with no DBSA and other regions with sulfur con-

tent close to that in neat DBSA (sulfur content in neat DBSA is 9.82 wt %) are found. Hence, even though the remaining DBSA content is low in the washed sample, a portion of it still appears as free DBSA. The conductive PANI(DBSA)_x complex content (assuming $x = 0.33$ to fit the doping level of PANI–OP–H₂SO₄), in the DBSA-rich surface layer is still low. The unwashed and washed samples with a 1 to 0.20 PANI-to-DBSA molar ratio (PANI–OP–DBSA-2, second kneading) behave similarly to PANI-OP-DBSA-1, except for the darker blue or black tinge color [Table IV, Fig. 2(c) and (d)]. In the unwashed samples of PANI–OP–DBSA-3 (1 to 0.39 PANI-to-DBSA molar ra-

Table III EDS Analysis of Sulfur Content

Sample	Accelerating Voltage (kV)	Average Scanning Depth (μm)	Sulfur Content	Error (1-Sigma)	Calculated Sulfur Content (wt %)
PANI–OP–DBSA (water-washed)	25	3.0	4.3	+/- 0.2	3.2
	15	1.5–2.0	6.4	+/- 0.7	
	5	0.5	7.9	+/- 3.0	
PANI–CL–DBSA (water-washed)	15	1.5		+/- 0.5	0.9
Versicon–DBSA (water-washed)	15	2.0	7.2	+/- 1.3	4.2
PANI–OP–DBSA–1 (water-washed)	15	2.0	2.2	+/- 0.5	2.3
	5	0.3–0.5	9.8	+/- 7.6	
	5	0.2–0.3	0.0	+/- 0.0	
PANI–DBSA complex ^a	15	1.5–2.0	8.3	+/- 2.2	7.5
	15	1.5–2.0	7.1	+/- 1.5	

^a Precipitate from filtrate after PANI–OP–DBSA–3 stirring with chloroform.

Table IV Redoping of PANI-OP-Base with DBSA

Sample	PANI-to-DBSA Weight Ratio	PANI-to-DBSA Molar Ratio	Appearance	Conductivity (S/cm)
PANI-OP-DBSA-1	1 : 0.54	1 : 0.15	Dark violet powder [Fig. 2(a)]	0.175
PANI-OP-DBSA-1 (water-washed)	1 : 0.31	1 : 0.086	Dark violet powder [Fig. 2(b)]	0.126
PANI-OP-DBSA-2	1 : 0.72	1 : 0.20	Violet-blue powder [Fig. 2(c)]	0.175
PANI-OP-DBSA-2 (water-washed)	PANI-OP-DBSA-1 + DBSA 1 : 0.36	1 : 0.100	Black-violet powder [Fig. 2(d)]	0.166
PANI-OP-DBSA-3	1 : 1.40	1 : 0.39	Dark blue powder [Fig. 2(e)]	0.063
PANI-OP-DBSA-3 (water-washed)	PANI-OP-DBSA-2 + DBSA 1 : 0.44	1 : 0.125	Dark green powder [Fig. 2(f)]	0.176
PANI-OP-DBSA-3 (acetone-washed)	1 : 0.20	1 : 0.05	Black-brown powder	0.050
PANI-OP-DBSA-3 (chloroform-washed)	< 1 : 0.14	< 1 : 0.04	Dark violet powder [Fig. 2(g)]	0.120
PANI-OP-DBSA-4	1 : 1.80	1 : 0.50	Grey-blue lumps	0.055
PANI-OP-DBSA-4 (water-washed)	PANI-OP-DBSA-3 + DBSA 1 : 0.66	1 : 0.185	Dark green powder [Fig. 2(d) and (f)]	0.380

tio, third kneading) and PANI-OP-DBSA-4 (1 to 0.5 PANI-to-DBSA molar ratio, fourth kneading), a large amount of free DBSA remains on the aggregates' surface [Fig. 2(e)], resulting in a lower conductivity (Table IV). However, the washed samples of PANI-OP-DBSA-3 and PANI-OP-DBSA-4 are dark green powders, containing slightly more DBSA and exhibiting a somewhat higher conductivity level compared to the water-washed PANI-OP-DBSA-1 and PANI-OP-DBSA-2. The appearance of these samples is similar to that of the washed PANI-OP-DBSA-2 sample [Fig. 2(f), Table IV]. Table IV shows that rinsing of the PANI-OP-DBSA-3 sample with acetone results in removal of larger amounts of DBSA in comparison with the water treatment. At the same time, the acetone washed PANI-OP-DBSA-3 had much higher conductivity level contrary to the acetone washed PANI-OP-DBSA (Tables IV and II, respectively). It may be concluded that the successive addition of increasing amounts of DBSA improve the PANI(DBSA)_{0.33} complex outer layer continuity.

The next step to further establish the hypothesis of the DBSA-rich surface layer structure of redoped powders was an attempt to dissolve the PANI(DBSA)_{0.33} complex thin outer layer and

free DBSA and obtain PANI-base aggregates. Magnetic stirring of PANI-OP-DBSA-3 with chloroform yielded a green suspension, which was filtered and washed with excess chloroform and then with acetone to remove residual amounts of DBSA and chloroform. The filtrate was precipitated by acetone to yield a complex of a dark blue color, of 7–8 wt % sulfur content (Table III). This sulfur value practically equals the content of 7.5 wt % sulfur in PANI-to-DBSA equal to 1 : 1 molar ratio, a proportion known to render solubility of PANI-DBSA in a given solvent.³ The washed and dried PANI-OP-DBSA-3 has a weight equal to the PANI-base content in the original PANI-OP-DBSA-3 and also a similar color to that of the PANI-base. The conductivity, however, is 0.12 S/cm, a level similar to that of all the previously water-washed samples and even the pristine PANI-OP-sulfate (Tables I, II, and IV). The actual quantity of the conducting PANI(DBSA)_{0.33} complex is rather small (Table IV). Thus, a continuous, very thin outer layer coating the aggregates of primary PANI particles [Fig. 2(g)], is sufficient to create a conducting network. It is proposed that a thin layer of about 5–10 nm thick creates a conducting network under compression molding within the chloroform-washed PANI-OP-

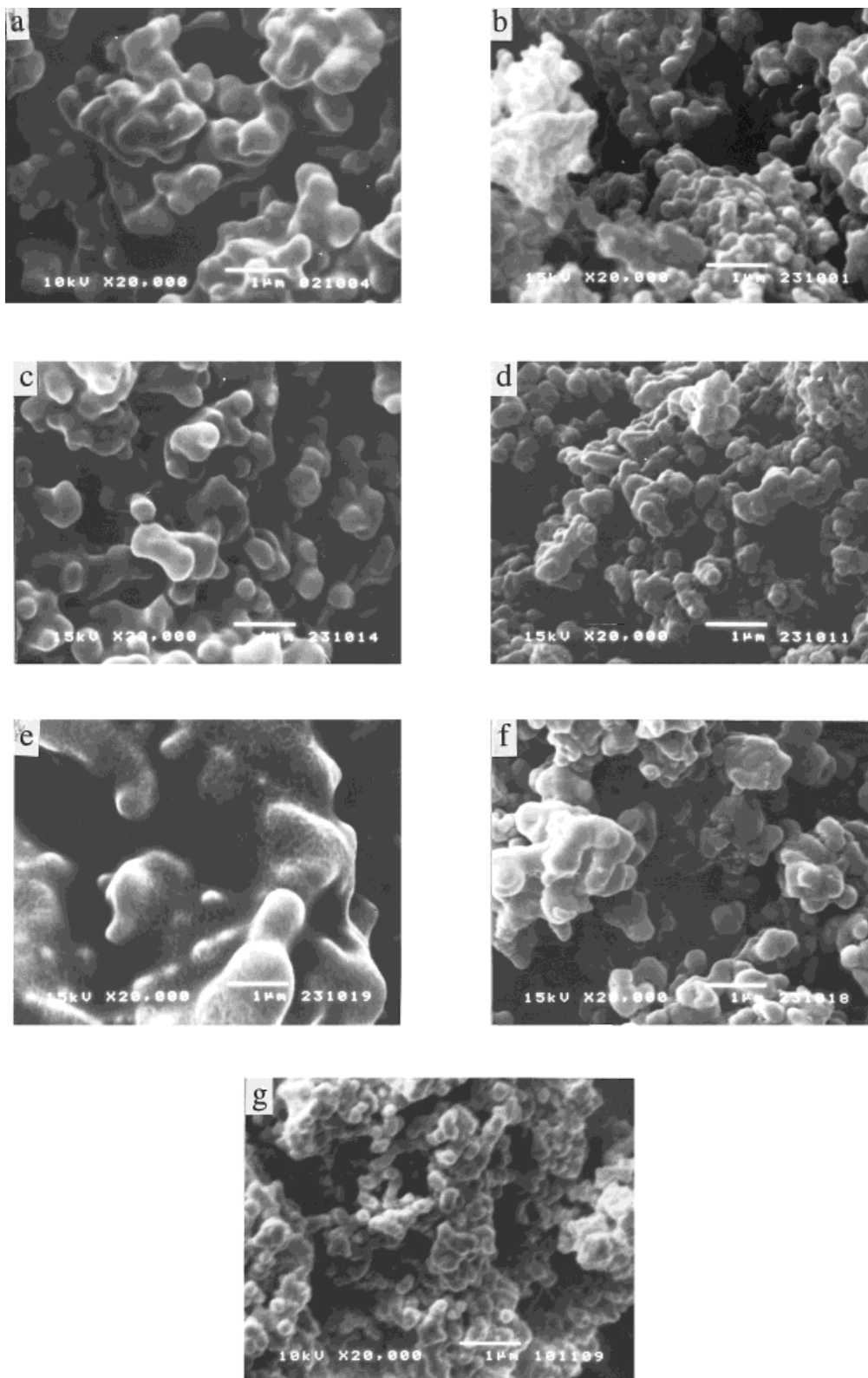


Figure 2 SEM micrographs of (a) PANI-OP-DBSA-1, (b) water-washed, PANI-OP-DBSA-1, (c) PANI-OP-DBSA-2, (d) water-washed PANI-OP-DBSA-2, (e) PANI-OP-DBSA-3, (f) water-washed PANI-OP-DBSA-3, and (g) chloroform-washed PANI-OP-DBSA-3. The designations correspond with Table IV.

DBSA-3 sample. It is apparent that the very thin surface layer is transparent, and the color of PANI-base aggregates is sometimes visible.

CONCLUSIONS

The redoping process of PANI-base powder with DBSA under mild conditions results in a mixture of undoped PANI, fully doped PANI-DBSA complex, and free DBSA. The mixture consists of PANI aggregates with DBSA-rich surface layer, where undoped PANI aggregates of primary particles of about 50–100 nm in size are covered by PANI(DBSA)_{0.33} outer layer. The excess DBSA, acting as a plasticizer, covers the conductive outer layer. It is suggested that, actually, a very thin conducting layer of fully doped PANI-DBSA complex of about 5–10 nm in size results in the conductivity of compression-molded samples by the formation of a three-dimensional conductive network. The thickness and continuity of the conductive network largely depend on the PANI aggregates' morphology, formed by the specific synthesis method and the conditions used.

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